VELOCITY-MAP IMAGING STUDY OF THE PHOTODISSOCIATION DYNAMICS OF HCl AND HBr

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The photodissociation dynamics of HCl and HBr molecules via low lying Rydberg and ion-pair states (2.0 - 2.5 eV below their respective ionization thresholds) was studied by using 2+1 REMPI spectroscopy and the velocity map imaging technique. One photon absorption by the unperturbed Rydberg states of both HCl and HBr leads to direct ionization to the ground state of the molecular ions, according to the Frank-Condon rule and with ionic core preservation. The photoionization of the ion-pair state or the Rydberg states interacting with the ion-pair state of HCl leads to the formation of a long vibrational progression of ground state molecular ions, via electronic autoionization of a gateway superexcited state [a]. In contrast, we found that for the one-photon excitation of the corresponding intermediate states of HBr the direct ionization pathway is favored. The competing channel, excitation of one or more superexcited states, leads almost exclusively to excited atomic fragments and not to molecular ions.

[a] C. Romanescu, S. Manzhos, D. Boldowsky, J. Clarke and H.-P. Loock, J. Chem. Phys., **120**, 767 (2004)